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### (54) EXHAUST GAS CATALYST

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(56) References cited:  
EP-A- 0 787 521 GB-A- 1 430 730  
GB-A- 2 149 680 US-A- 4 221 768  
US-A- 4 466 947 US-A- 4 719 192  
US-A- 5 300 472

- PATENT ABSTRACTS OF JAPAN vol. 0030, no. 75 (C-050), 27 June 1979 (1979-06-27) & JP 54 052691 A (NIPPON STEEL CORP), 25 April 1979 (1979-04-25)
- PATENT ABSTRACTS OF JAPAN vol. 1999, no. 13, 30 November 1999 (1999-11-30) & JP 11 216361 A (TOSHIBA CORP), 10 August 1999 (1999-08-10)

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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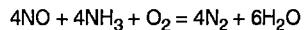
## Description

[0001] The invention relates to an exhaust gas catalyst composition, in the following "catalyst composition", and a process for its preparation.

5 [0002] The reduction of nitrogen oxide emissions represents one of the greatest challenges in environmental protection. Several approaches have been followed to reduce  $\text{NO}_x$  emissions for both mobile and stationary applications including combustion modification methods and denitrification of flue gases. The former, although  $\text{NO}_x$  removal efficiency varies with the technology applied, cannot achieve more than 50-60% of removal efficiency. After-treatment of flue gases can achieve substantially larger efficiencies especially when a catalytic method is employed. Several type of catalysts have  
10 been tested which are active under different environments and conditions. The use of a large number of catalysts to eliminate NO is associated with different reaction pathways that can be divided as follows (1):

1. The selective catalytic reduction of NO with ammonia (herein after referred to as SCR), for stationary applications like power stations and chemical industrial plants.
- 15 2. The catalytic reduction of NO in the presence of CO, typical of automotive pollution control.
3. The catalytic reduction of NO in the presence of hydrocarbons, a method not in use commercially but potentially interesting for automotive and industrial pollution control.
4. The direct elimination of NO through decomposition for which a durable and stable catalysts has not yet been developed.
- 20 5. The sorbing of NO or  $\text{NO}_x$ -trap catalysts.

25 [0003] Among these methods the most widely employed technology for stationary applications is SCR (2-4). It was introduced in the late 1970s for the control of  $\text{NO}_x$  emissions in stack gases for thermal power plants and other industrial facilities. SCR plants are currently operating in USA, Japan, Europe and Far East for a total capacity of the order of 180000 MW. The SCR is based on the reduction of  $\text{NO}_x$  with  $\text{NH}_3$  into water and nitrogen according to the reaction:



30 [0004] The technology is operated commercially over metal-oxide SCR catalysts made of a homogeneous mixture of  $\text{TiO}_2$  (80-90 wt.-%),  $\text{WO}_3$  (6-10 wt.-%) and  $\text{V}_2\text{O}_5$  (up to 3 wt.-%) which may contain some  $\text{SiO}_2$  (0-10 wt.-%) in the formulation. Titania is used as an active support of high surface area to support the active component  $\text{V}_2\text{O}_5$  which is responsible for the activity of catalysts for  $\text{NO}_x$  reduction at low and medium operation temperatures. It is also responsible for the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  when  $\text{SO}_2$  containing gases are delivered to the catalyst. Therefore, for high-sulfur content off-gases, its amount is kept low (below 1 wt.-%).  $\text{WO}_3$  (sometime also  $\text{MoO}_3$ ) is employed as a chemical/35 structural promoter to enlarge the temperature window of application. Silica is often used to improve the catalyst strength and stability. Commercial catalysts are employed as honeycomb monoliths due to several advantages over a packed bed arrangement: lower pressure drop, higher attrition resistance, less plugging by fly ash.

40 [0005] GB 1 495 396 describes a catalyst composition containing as active ingredients oxides from titanium, at least one of molybdenum, tungsten, iron, vanadium, nickel, cobalt, copper, chromium and uranium, and as optional component (s) tin and/or at least one of silver, beryllium, magnesium, zinc, boron, aluminium, yttrium, rare earth metal, silicon, niobium, antimony, bismuth, manganese, thorium and zirconium, which oxides are present as an intimate mixture.

45 [0006] EP I 145 762 A1 describes a process for the preparation of a vanadia SCR-catalyst supported on titania. The process is characterized in that the catalyst is prepared by dispersing titania in an ammonium metavanadate solution, adjusting the pH of the solution to a value of 7.0-7.1, stirring the resulting suspension for a time for complete adsorption of the vanadium compound on titania, filtering the suspension and drying and calcining the resulting catalyst compound.

50 [0007] From US 4,466,947 a denitrification catalyst is known comprising at least the three metal components titanium, tungsten and/or magnesium, and vanadium, and may contain additionally a plurality of metal elements of the periodic system.

[0008] From PATENT ABSTRACTS OF JAPAN; vol. 0030, no. 75 (C-050), 27 June 1979 & JP 54 052691 A, 25 April 1979 a catalyst for removing nitrogen oxides in exhaust gases is known consisting of  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and oxides of lanthanides.

55 [0009] In spite of the fact that SCR technology is used worldwide there are still opportunities to improve catalytic performance especially in relation to the following issues: (i) to improve catalyst design in order to obtain at the same time a higher activity in  $\text{NO}_x$  removal and a lower activity in  $\text{SO}_2$  oxidation; (ii) to limit ammonia slip and to improve the behaviour of the system under dynamic conditions; (iii) to extend the present applicable temperature range of SCR catalysts towards higher temperature up to 600°C and to avoid deactivation which occurs at present catalysts when operated at high temperatures. It is in fact known that the activity of a  $\text{V}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$  catalyst increases markedly with a rise in calcinations temperature up to 600-650°C and then rapidly decreases. This is mainly due to phase transformation of  $\text{TiO}_2$  (anatase) into  $\text{TiO}_2$  (rutile) and consequent loss of BET surface area with changes in the chemical state of surface

vanadium species. Solving these issues will pave the road for use of SCR also in mobile applications; the process using urea as reducing agent is in fact investigated intensively for use in diesel or gasoline lean-burn engines (5-6). The challenges for automotive applications are high SCR activity and improved thermal stability of vanadia-tungsta-titania catalysts in the temperature range 423-1000K. Such extreme operating temperatures (compared to "classic" SCR applications where temperature range of the order of 573-773K are often encountered) are certainly of short duration and may occur at very high power output (low rpm and high load).

5 [0010] The present invention is aimed to solve the problem related to improvement of thermal stability at higher temperatures where state of the art V/Ti/W/Si and V/Ti/W catalysts still suffer strong deactivation.

10 [0011] The process according to the invention for the preparation of a catalyst composition is characterized in that a solid support containing  $\text{TiO}_2$  in an amount of at least 70 wt.-%,  $\text{WO}_3$  in an amount of 5-20 wt.-%, and optionally  $\text{SiO}_2$  in an amount of up to 15 wt.-%, is contacted with a vanadate (REVO<sub>4</sub>) of at least one rare earth metal selected from the group of Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Yb to give a slurry which is brought to dryness and calcined. By bringing the solid support in contact with the rare earth vanadate, adsorption on the support takes place.

15 [0012] In a more preferred embodiment the rare earth metal is at least one of the group of Pr, Sm, Gd, Tb, Dy and Er, and particularly one of the group of Sm, Gd, Tb, Dy and Er, and more preferred at least one of Er and Tb.

[0013] The invention is also directed to a catalyst composition which is obtainable according to the inventive process mentioned above.

[0014] In the following preferred embodiments of the invention are described in more detail.

20 [0015] The support of the catalyst composition preferably contains  $\text{SiO}_2$  in an amount of 4-12 wt.-%, particularly in an amount of 5-10 wt.-%.

### 1. Preparation of a catalyst according to the invention containing 5.0 wt.-% Er and 1.5 wt.-% V on a Ti-W-Si support

#### 1.1. Preparation of the Ti-W-Si support

25 [0016] Preparation of the support was carried out according to (7): 92.68g of titanium tetrachloride ( $\text{TiCl}_4$ ) was added dropwise to 1 liter of water under ice cooling with stirring. Then 16.06g of Lithosol 1530 KD (a tradename for a product of Zschimmer & Schwarz Chemische Fabriken, containing 30% of  $\text{SiO}_2$  in the sol state) were added. While thoroughly stirring the mixture at about 30°C, ammonia water was gradually added. When the pH of the mixture reached 7, the addition was stopped. The mixture was aged by allowing it to stand for 2 hours. The resulting  $\text{TiO}_2$ - $\text{SiO}_2$  gel was filtered, washed with water, dried at 120°C for 10 hours and further washed with water, then calcined at 500°C for 3 hours. The resulting  $\text{TiO}_2$ - $\text{SiO}_2$  powder contained 86 mole% of titanium and 14 mole% of silicon as  $\text{SiO}_2$ . The resulting powder was designated as (Ti/Si).

30 [0017] A solution of 8.16 g of ammonium paratungstate  $[(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}]$  in 500 ml of distilled water was added to 73.4g of (Ti/Si). They were thoroughly mixed with stirring, concentrated, dried and calcined at 500°C for 6 hours. The resulting support had a weight% ratio  $\text{TiO}_2:\text{WO}_3:\text{SiO}_2$  of 81:9:10.

#### 1.2. Preparation of the catalyst according to the invention

##### 40 1.2.1 Preparation of the Erbiumvanadate (ErVO<sub>4</sub>)

[0018] The crystalline ErVO<sub>4</sub> is prepared by the liquid - phase reaction method. 1.032 g of  $\text{NH}_4\text{VO}_3$  are dissolved in distilled water at 80°C in order to obtain a 0.1 mol/l solution; at the same time an Erbium Nitrate Solution (0.2 mol/l) is prepared by diluting 6.695 g of  $\text{Er}(\text{NO}_3)_3$  solution (containing 22.16% of Er) with distilled water at 80°C.

45 After mixing the two solutions under continuous stirring the pH was adjusted to 7.0 with the help of ammonia (30% solution). This causes the precipitation of a white-pale pink compound (EbVO<sub>4</sub>) that was filtered, washed several times with distilled water and dried at 100°C overnight.

##### 50 1.2.2. Preparation of the catalyst

[0019] Two slurries were formed dissolving 252.3 mg of ErVO<sub>4</sub> and 2747.7 mg of the Ti/W/Si support ( $\text{WO}_3/\text{TiO}_2$ -(10%)  $\text{SiO}_2$ ) in distilled water. The two slurries were mixed heating up to 90°C and stirring. The final slurry was brought to dryness under continuous stirring at 80-100°C. Finally, the solid was dried at 120°C overnight and calcined at 650°C for 2 hours, pressed into pellet, crushed and sieved in the range 355-425  $\mu\text{m}$ . This will be referred as fresh sample.

55 Aging of samples was carried out in a tubular furnace at a temperature of 750°C for 10 hours under air.

## 2. Preparation of a state of the art catalyst 1.7%V/Ti/W (8)

## 2.1. Preparation of the Ti-W support

5 [0020] The preparation of the support was carried out according to (9) : 87g of titanium tetrachloride ( $TiCl_4$ ) were poured into 300 ml of ice water and the solution was neutralized with 3N ammonia water. The resulting precipitate was separated by filtration, and thoroughly washed with distilled water. A solution of 4.58g of ammonium paratungstate  $[(NH_4)_10W_{12}O_{41} \cdot 5H_2O]$  in 325 ml of distilled water was thoroughly mixed with the resulting cake. The resulting slurry was dried, and calcined at 500°C for 6 hours in a muffle furnace. The resulting support had a weight% ratio  $TiO_2:WO_3$  of 90:10.

## 2.2. Preparation of the catalyst 1.7%V/Ti/W

15 [0021] An aliquot of 77.2 mg of ammonium metavanadate was dissolved in 10 ml of 1N oxalic acid. The solution was heated in order to obtain the blue complex  $(NH_4)_2[VO(C_2O_4)_2]$ . Then, the support (1940 mg of mixed oxide containing 90% $TiO_2$ -10% $WO_3$ ) was added. This slurry was brought to dryness under continuous stirring at 80-100°C. Finally, the solid was dried at 120°C overnight and calcined at 650°C for 2 hours, pressed into pellet, crushed and sieved in the range 355-425  $\mu m$ .

20 [0022] The specific surface areas of oxide powders were measured by the BET method using  $N_2$  adsorption/desorption at 77K with a Sorptomatic 1990 instrument (Carlo Erba).

## 3. Catalyst Testing

25 [0023] Catalyst testing was carried out in the apparatus described in Figure 1. The gas feed consisted of  $NH_3/N_2$ ,  $NO/N_2$ ,  $O_2$ ,  $N_2$ . Mass flow meters were used to measure and control the single gaseous stream while an injection pump was used to introduce water. The feed stream was preheated and premixed and ammonia was added to the gaseous mixture immediately before entering the reactor to avoid side reactions. A tubular quartz reactor was employed inserted in a furnace. Temperature was controlled by a thermocouple inserted in the catalyst bed. The gas exiting the reactor was scrubbed with an aqueous solution of phosphoric acid to trap unconverted ammonia and then cooled to condense water vapor. Activity of the catalysts were measured under stationary conditions in a temperature range of 250°C to 450°C. Unless otherwise reported the standard gas composition and reaction conditions given in Table 1 were used. Conditions were selected in order to have a conversion not exceeding ca. 90% with reference catalyst. Gas composition analysis was carried out with an FTIR spectrometer equipped with a gas cell.

35 [0024] Table 2 shows NOx removal efficiency in the temperature range 250-450°C for catalysts prepared according to the invention process containing 0.4-2.1 wt.% V and 1.4-5.1 wt.% RE on Ti/W/Si support. For comparison the activity of the state of the art reference catalyst based on 1.7 wt.% V/Ti/W are also reported.

40 [0025] The  $NO_x$  reduction activity of all the catalysts examined in the present study increased with increasing reaction temperature up to about 320°C where a maximum  $NO_x$  reduction activity was observed. At this point the activity began to decrease due to lower ammonia adsorption capacity. A strong effect is also shown with aging (calcination at 750°C for 10 h). Particularly for the state of the art catalyst calcined at a temperature of 750°C strong deactivation is observed with conversion dropping at values between 5-20%. A similar strong deactivation is observed also with La-containing catalyst. All the other catalysts can be broadly divided in two groups: group A catalysts (comprising Y,Ce,Pr and Nd) which suffer a slight deactivation after ageing and group B catalysts (comprising Sm, Gd, Tb, Dy, Er, -Yb is in the middle of the two groups-) in which deactivation has no effect or even causes an improvement of overall efficiency. The best performances are observed with Er and Tb containing catalysts where a substantial increase of conversion is observed after ageing in all temperature range examined.

Table 1: Reaction conditions and gas composition

50	Catalyst weight	100,0 mg
	Particle size	350-425 $\mu m$
	Total flow	0,3 l/min
	Temperature	250-450°C
55	NO conc.	200 ppm
	NH <sub>3</sub> conc.	240 ppm

(continued)

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O <sub>2</sub> conc.	20000 ppm
H <sub>2</sub> O conc.	10%
N <sub>2</sub> conc.	balance

Table 2: Activity of fresh and aged catalysts prepared according to the inventive process containing RE and V on TiO<sub>2</sub>; WO<sub>3</sub>:SiO<sub>2</sub> (81:9:10) matrix

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Example Nr	RE	RE [%]	V [%]	250°C fresh	250°C aged	320°C fresh	320°C aged	450°C fresh	450°C aged
1	Tb	4,9	1,6	31	50	53	77	36	33
2	Er	5	1,5	33	73	75	91	64	46
(Reference)	-	-	1,7	85	5	91	17	17	7

**References:**

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[0026]

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1. V. I. Parvulescu, P. Grange, B. Delmon, Cat. Today 46 (1998) 233.
2. P. Forzatti, Appl. Catal. A: General 222 (2001) 221
3. S.E. Park, G.M. Kim, Y.J. Lee, J.S. Chang, S.H. Han, US Patent 5879645 (1999).
4. P.S.Ji, H.M.Eum, J.B.Lee, D.H.Kim, I.Y.Lee, I.S.Nam, S.W.Ham, S.T.Cho, US Patent 6380128 (2002)
5. G. Madia, M. Elsener, M. Koebel, F. Raimondi, A. Woukan, Applied catalysis B: Environmental 39 (2002) 181.
6. M. Koebel, M. Elsener, M. Kleeman, Catal. Today 59 (2000) 335.
7. A. Inoue, T. Suzuki, K. Saito, Y. Aoki, T. Ono, T. Ohara, US patent 4221760 (1980).
8. A. Schafer-Sindlinger, A. Burkhardt, H. Van der Tillaart, T. Kreuzer, E. Lox, W. Weisweller, Eu Patent Application EP 1 145762 A1
9. GB. Patent. 1495396 (1974); Mitsubishi Petrochemical Co. Ltd.
10. R. Y. Saleh, I. E. Wachs, S. S. Chan, C. C. Chersich, J. Catalysis 98 1(986) 102.
11. I. Nova, L. dall'Acqua, L. Liotti, E. Giamello, P. Forzatti, Applied Catalysis B: Environmental 35 (2001) 31.

**Claims**

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1. A process for the preparation of a catalyst composition, characterized in that a solid support containing TiO<sub>2</sub> in an amount of at least 70 wt.-%, WO<sub>3</sub> in an amount of 5-20 wt.-%, and optionally SiO<sub>2</sub> in an amount of up to 15 wt.-% is contacted with a vanadate (REVO<sub>4</sub>) of at least one rare earth metal selected from the group of Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Yb to give a slurry which is brought to dryness and calcined.
2. Catalyst composition obtainable according to a process of claim 1.

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**Patentansprüche**

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1. Verfahren zur Herstellung einer Katalysatorzusammensetzung, dadurch gekennzeichnet, dass ein fester Träger, enthaltend TiO<sub>2</sub> in einer Menge von mindestens 70 Gew.-%, WO<sub>3</sub> in einer Menge von 5-20 Gew.-% und gegebenenfalls SiO<sub>2</sub> in einer Menge von bis zu 15 Gew.-%, mit einem Vanadat (REVO<sub>4</sub>) mindestens eines Seltenerdmetalls, ausgewählt aus der Gruppe von Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er und Yb, kontaktiert wird, um einen Schlamm zu ergeben, der zur Trockenheit gebracht und kalziniert wird.
2. Katalysatorzusammensetzung, erhältlich gemäß einem Verfahren nach Anspruch 1.

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**Revendications**

1. Procédé pour la préparation d'une composition de catalyseur, **caractérisé en ce qu'un support solide** contenant du TiO<sub>2</sub> dans une quantité d'au moins 70% en poids, du WO<sub>3</sub> dans une quantité de 5 à 20% en poids, et facultativement du SiO<sub>2</sub> dans une quantité de jusqu'à 15% en poids est mis en contact avec un vanadate (REV04) d'au moins un métal des terres rares choisi parmi le groupe de Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er et Yb pour donner une suspension épaisse qui est amenée à sécheresse et calcinée.
2. Composition de catalyseur pouvant être obtenue conformément à un procédé selon la revendication 1.

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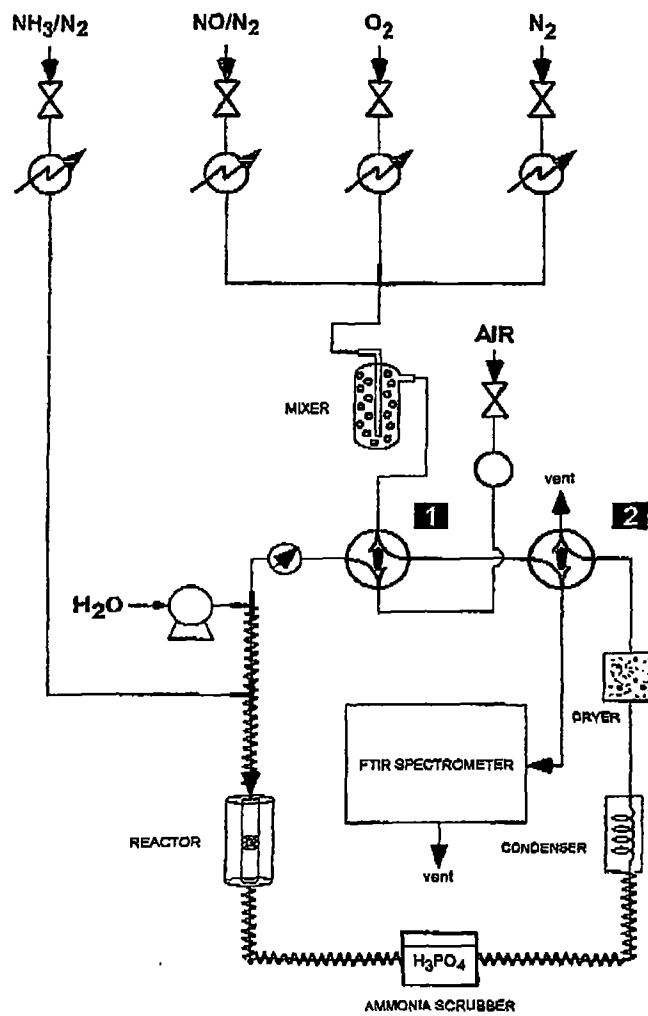


Figure 1: Scheme of the apparatus

REFERENCES CITED IN THE DESCRIPTION

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**Patent documents cited in the description**

- GB 1495396 A [0005] [0026]
- EP 1145762 A1 [0006]
- US 4466947 A [0007]
- JP 54052691 A [0008]
- US 5879645 A, S.E. Park, G.M. Kim, Y.J. Lee, J.S. Chang, S.H. Han [0026]
- US 6380128 B, P.S.Ji, H.M.Eum, J.B.Lee, D.H.Kim, I.Y.Lee, I.S.Nam, S.W.Ham, S.T.Cho [0026]
- US 4221760 A, A. Inoue, T. Suzuki, K. Saito, Y. Aoki, T. Ono, T. Ohara [0026]
- EP 1145762 A1 [0026]

**Non-patent literature cited in the description**

- PATENT ABSTRACTS OF JAPAN, 27 June 1979, vol. 0030, 75 (C-050) [0008]
- V. I. Parvulescu ; P. Grange ; B. Delmon. *Cat. Today*, 1998, vol. 46, 233 [0026]
- P. Forzatti. *Appl. Catal. A: General*, 2001, vol. 222, 221 [0026]
- G. Madia ; M. Elsener ; M. Koebel ; F. Raimondi ; A. Woukan. *Applied catalysis B: Environmental*, 2002, vol. 39, 181 [0026]
- M. Koebel ; M. Elsener ; M. Kleeman. *Catal. Today*, 2000, vol. 59, 335 [0026]
- R. Y. Saleh ; I. E. Wachs ; S. S. Chan ; C. C. Chersich. *J. Catalysis*, vol. 98, 102 [0026]
- I. Nova ; L. dall'Acqua ; L. Lietti ; E. Giannello ; P. Forzatti. *Applied Catalysis B: Environmental*, 2001, vol. 35, 31 [0026]